



Oxidative degradation of acid doped polybenzimidazole membranes and fuel cell durability in the presence of ferrous ions

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HIGHLIGHTS

- Oxidative degradation of PBI membranes investigated under Fenton radical attacks.
- Accelerating effect of ferrous ions on the polymer degradation confirmed.
- Suppressing effect of phosphoric acid on the polymer degradation first reported.
- Durability tests verified the positive effect of the acid under ferrous contamination.

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ABSTRACT

Phosphoric acid doped polybenzimidazole membranes have been explored as proton exchange membranes for high temperature polymer electrolyte membrane fuel cells. Long-term durability of the membrane is of critical concern and has been evaluated by accelerated degradation tests under Fenton conditions. In this study effects of phosphoric acid and ferrous ions were investigated by measurements of the weight loss, intrinsic viscosity and size exclusion chromatography (SEC) of the polymer membranes. Ferrous ions resulted in, as expected, catalytic formation of peroxide radicals and hence the accelerated polymer degradation in terms of weight loss and molecular weight decrease. The presence of phosphoric acid as an inevitable dopant of the membranes, on the other hand, significantly impeded the membrane degradation by means of metal ion complexing, decreased pH, and acid–base interactions with the amino groups of the polymer. Fuel cell durability tests with contaminations of ferrous ions did show considerable performance degradation, however, primarily due to the catalyst deterioration rather than the membrane degradation.

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1. Introduction

Great efforts are being made to develop proton conducting membranes and other materials for proton exchange membrane fuel cells (PEMFC) with an operational temperature above 100 °C. The advantages include enhanced fuel impurity tolerance, eliminated water management and simplified cooling. [1] To achieve a high temperature operation under ambient pressure, phosphoric acid (PA) doped polybenzimidazole (PBI) membranes were proposed [2]. Fuel cells based on the membranes have been

demonstrated with operational features of no mandatory humidification [3], high CO [4] and SO₂ [5,6] tolerance, better heat utilization [7,8] and possible integration with fuel processing units [9,10], as recently reviewed [11].

The most significant challenge for PBI membranes and fuel cells is the life time, where 40,000 h of operation for stationary uses and 5000 h of operation for automobile uses are required with most preferably less than 10% of performance decay. Operating with hydrogen and air, a life time of over 20,000 h has been demonstrated at 160 °C [5,12]. From the result, a degradation rate of the cell performance is estimated to be about 5–6 μV h^{−1}. Similar results were reported by Yu et al. [13], showing a voltage degradation rate of 4.9–6.3 μV h^{−1} at 160 °C. Based on acid doped AB-PBI

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membranes, Wannek et al. [14] reported a high degradation rate of 20–25 $\mu\text{V h}^{-1}$ under a constant load. Both Yu et al. [13] and Wannek et al. [14] have tried to collect the acid from the off-gases of the fuel cells and found the phosphoric acid loss rate in the range from 0.03 to 0.2 $\mu\text{g m}^{-2} \text{s}^{-1}$. This very low acid loss rate, corresponding to a total acid loss of a few percents of the acid content in the membranes after 40,000 h of steady state operation, was also confirmed by the nearly constant ohmic resistance of the cells through the test period. In addition, Lobato et al. [15,16] demonstrated that fuel cells operating with titanium-based composite membranes showed a better stability during the preliminary long-term test because of the better acid retention capability.

It should be noted that this low performance degradation rate was achieved under a steady state operation at 150–160 °C. Under these circumstances no liquid water formation is involved. Another advantage of the steady state operation is the small change in the cell voltage. Any exposure to a high cell voltage would significantly increase the corrosion of the catalyst support, dissolution of the noble metal particles, and the oxidative degradation of the polymer membrane.

During dynamic tests with thermal, load and shutdown-startup cycling, more challenges arise for the fuel cell component durability [14]. The amount and the vapour pressure of the water product vary and formation of liquid water might be involved. In addition, the shutdown-startup or/and temperature cycling cause thermal and mechanical stresses to the membranes as the volume expansion and contractions occur. More importantly, the dynamic cycling periodically brings the MEA to high cell voltages, which in turn impose significant oxidative degradation of membranes, catalysts and other MEA and cell construction materials. A thermal and load cycling test on a hydrogen-air cell with a daily shutdown and restart over a period of more than 3 years with more than 850 cycles showed an average performance loss of 0.3 mV per cycle [11]. Based on the commercial Celtec®-P1000 MEA, Calundann [17] and Schmidt et al. [5] reported a similar daily startup-shutdown cycling test, also with an average voltage drop of 0.3 mV per cycle.

Oxidative degradation of the polymer and the failure of membranes have been recognized as one of the most important mechanisms for low temperature PEMFC failures. Extended investigations have been carried out for perfluorinated sulfonic acid membranes (e.g. Nafion®). H_2O_2 has been detected as an intermediate product of oxygen diffusing through the membrane and being incompletely reduced at the fuel cell anode [18,19]. Originating from decomposition of hydrogen peroxide, the attack of hydroxyl ($\text{HO}\cdot$) and hydroperoxy ($\text{HOO}\cdot$) radicals is proposed to be a principal degradation mechanism of polymer membranes [20,21]. Experimentally the peroxide radicals can be generated by the decomposition of H_2O_2 with transition metal ions, e.g. Fe^{2+} , as a catalyst. By exposing a membrane to a hydrogen peroxide solution containing Fe^{2+} , the so-called Fenton test has been widely used for stability evaluation of PEMFC membranes. In real fuel cells in operation, Kinumoto et al. [22], for example, investigated the durability of Nafion membranes in the presence of hydrogen peroxide containing transitional metal ions. As a result of catalyzed decomposition of the peroxide in the presence of Fe^{2+} or Cu^{2+} ions, significantly increased degradation of the membranes was observed. These Fe^{2+} or Cu^{2+} ions, as typical contaminants and corrosion products of fuel cell construction materials such as bipolar plates, humidifiers, tubing, etc [23], are considered critical issues for the PEMFC durability.

For PBI membranes used in high temperature PEMFCs, degradation mechanisms under atmospheric [24–26] and radical [27–31] oxidation have been studied. During the Fenton test, significant weight losses were observed, depending on the initial molecular weight of the polymer. At the same time, a steady decrease

in the average molecular weight of the polymer occurred as revealed by the viscosity and size extrusion chromatography (SEC) measurements [27]. Based on FTIR spectra and other observations of PBI samples after Fenton test as well as the following heat treatment at up to 400 °C, mechanisms of oxidative degradation of PBI was suggested [27]. Most of these studies were carried out on pristine PBI membranes without taking into account the effect of the inevitable doping phosphoric acid, which is however proposed to play an important role in the polymer degradation [32]. The present work is devoted to further investigation of the oxidative degradation of PBI membranes by means of the Fenton test and fuel cell durability in the presence of phosphoric acid and ferrous ions.

2. Experimental

2.1. Materials

PBI was synthesized from 3,3'-4,4'-tetraaminobiphenyl (TAB) and isophthalic acid (IPA), as described previously [30]. Dimethylacetamide (DMAc, HPLC grade), H_2O_2 , phosphoric acid (85 wt%), $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ were all from Sigma–Aldrich. All chemicals were used as received without further purification.

2.2. Fenton test in the absence and presence of phosphoric acid

Dry PBI membranes (ca. 80 μm) with a size of about 2 cm^2 and a weight of about 0.4 g each were immersed in a 50 ml Fenton solution consisting of 3 wt% H_2O_2 and typically 4 ppm Fe^{2+} (in form of $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$). The Fenton solution and the membrane samples were contained in a glass bottle with a gas tight cap and placed in a preheated oven at 68 °C. For about every 20 h, the Fenton solution was replaced with a freshly prepared one. After a certain period of time, the membrane samples were taken out of the bottle when it was in a whole piece or collected by filtering when it was broken into small pieces, washed thoroughly with distilled water, and dried at 120 °C for at least 12 h in the glass bottle. The bottle was capped before it was taken out of the oven to prevent the membrane samples from adsorbing moisture during the weighing in order to determine the weight loss due to the polymer oxidation.

For tests in the presence of phosphoric acid in the Fenton solution, a parallel membrane sample was used by immersing it in an aqueous solution containing the same amount of the acid but without hydrogen peroxide or ferrous ions. The weight gain of the reference sample, due to the acid doping, was used to correct the weight loss due to the polymer oxidation.

2.3. Viscosity

A polymer solution was first prepared by dissolving 0.2–1.0 g PBI powder in 100 ml 96 wt% H_2SO_4 under stirring at room temperature. After filtering, the viscosity of the solution was measured in a thermostat bath at 30 ± 0.02 °C using a Cannon Ubbelohde capillary dilution viscometer (Coneccta S.A.). The flow time of the solution between two marks of the capillary tube was recorded and the specific viscosity η_{sp} was calculated as follows:

$$\eta_{\text{sp}} = (\eta_{\text{c}} - \eta_{\text{o}})/\eta_{\text{o}} = (t_{\text{c}} - t_{\text{o}})/t_{\text{o}} \quad (1)$$

where t_{c} and t_{o} were the flow time of the polymer solution and pure solvent, respectively. The intrinsic viscosity, η_{IV} , was then obtained by plotting η_{sp}/C against C and extrapolating to $C = 0$ where C , in g dL^{-1} , was the polymer concentration in sulphuric acid solutions. The intrinsic viscosity is related to the average PBI molecular weight (M_{w}) by the Mark–Houwink–Sakurada expression:

$$\eta_{IV} = K \cdot M_w^\alpha \quad (2)$$

where K and α are empirical constants and taken as $K = 1.94 \times 10^{-4}$ and $\alpha = 0.791$ [27,33].

2.4. SEC measurement

Size exclusion chromatography (SEC) experiments were carried out at 40 °C by using a LC-10AD liquid chromatograph (Shimadzu), and a RID-10A Refractive index detector. In this instrument a high-resolution column setup was used, with 7 columns having a pore size range from 10^2 to 10^6 Å. DMAc with 0.5 wt% LiCl was used as the carrier solvent at a flow rate of 0.2 ml min^{-1} . Since the amount of the injected polymer influenced the peak elution volume, especially for the higher molecular weight samples, the same concentration (1.0 mg ml^{-1}) was used for all the polymer solutions. The weight averaged molecular weight (M_w) of the polymers were calculated from the retention time (t) of SEC using the following equation [27]:

$$\text{Log } [M_w] = -0.3004 t + 8.4524 \quad (3)$$

For studying the stability of hydrogen peroxide, a set of SEC measurements were conducted on 3 wt% H_2O_2 without and with addition of ferrous ions (of 4 ppm) and phosphoric acid (of 0.2 M).

2.5. FTIR spectroscopy

Fourier transform infrared spectra (FTIR) were recorded using a 1710 Infrared Fourier transform spectrometer for the two monomers for PBI synthesis, i.e. 3,3'-4,4' tetraaminobiphenyl (TAB) and isophthalic acid (IPA) before and after the radical oxidation in the Fenton solution. The Fenton solution was the same that used for the membrane tests, i.e. 3% H_2O_2 containing 4 ppm Fe^{2+} and the test temperature was 68 °C. 0.3 g of each monomer (TAB or IPA) was initially added into 40 ml of the Fenton solution. After 20 h the monomer samples were collected by filtration for the FT-IR spectroscopic measurements.

2.6. Fuel cell durability test

Non-woven carbon gas diffusion layers were first coated with a micro-porous carbon layer, onto which platinum catalysts supported on carbon black (56.2 wt% Pt/C) were sprayed with PBI as the catalyst binder. Phosphoric acid was then added into the catalyst layer to make the polymer phase conductive. The Pt loading of the final electrodes was 0.58 mg cm^{-2} for each electrode. For investigation of the Fe^{2+} effect on the membrane degradation as well as the fuel cell durability, ferrous ions in form of $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ were impregnated into the catalyst layer of electrodes. This ammonium ferrous double salt, also called Mohr's salt, was used as it is much less prone to the atmospheric oxidation of ferrous ions to ferric ions. Introduction of the ammonium salt may result in precipitation of ammonium phosphate. This is however not considered to have any significant effect on the result in the present situation when the overall content of the ammonium ferrous salt was limited to the ppm level. Thus impregnated electrodes contained ferrous ions of $0.5 \mu\text{g cm}^{-2}$. PBI membranes with an acid doping level of 11.2 mol H_3PO_4 were used for the fuel cell tests. In the present work, a relatively thick membrane, with a thickness of ca. 80 microns before acid doping and ca. 130 microns after doping, was used. With a polymer density of 1.3 g cm^{-3} the ferrous ion content in the catalyst layer was estimated to be ca. 50 ppm Fe^{2+} in PBI based on a mass ratio. The MEAs were prepared by hot-pressing at 155 °C under a pressure of about 70 kg cm^{-2} for

7 min. The active electrode area of the MEAs was 10 cm^2 . Single cells were assembled using two graphite plates with simple parallel gas channels. Two end plates made of aluminium with attached heaters were used to clamp the graphite plates and silver coated current collectors were used to collect the current from the cell. For all fuel cell tests, hydrogen and air at flow rates of 120 and 240 ml min^{-1} , respectively, were used without pre-humidification.

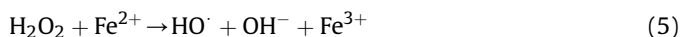
3. Results and discussion

3.1. Effects of phosphoric acid and ferrous ions on H_2O_2 decomposition

To examine decomposition of hydrogen peroxide in the absence and presence of ferrous ions and phosphoric acid, a set of SEC spectra were recorded, as shown in Fig. 1. The H_2O_2 solution showed two adjacent peaks, one at 18.6 min for H_2O and the other at 18.2 min for H_2O_2 . This was confirmed by the single peak observed for pure water at 18.6 min. Being held at 68 °C for 4 h under the ambient atmosphere, the peroxide peak at 18.2 min was decreased, indicating the decomposition of hydrogen peroxide:



When 4 ppm ferrous ions were added in the peroxide solution, also after 4 h at 68 °C, the decomposition was accelerated and the peroxide peak further decreased to about half of the height for the initial hydrogen peroxide solution. It is well known that, in the Fenton solution, the Fe^{2+} accelerates the decomposition of H_2O_2 (Reaction (4) above) which is accompanied by formation of active oxygen radicals of $\cdot\text{OH}$ and $\cdot\text{OOH}$ through the so-called Haber–Weiss mechanisms [22]:



As a result, after about 20 h, the decomposition seemed complete when the peroxide peak disappeared and the SEC curve was almost coincided with that of pure water with a single peak at 18.6 min.

In the following study, phosphoric acid was added into the Fenton solution, consisting of 3 wt% hydrogen peroxide and 4 ppm Fe^{2+} , to reach a total concentration of 0.2 M H_3PO_4 . The presence of

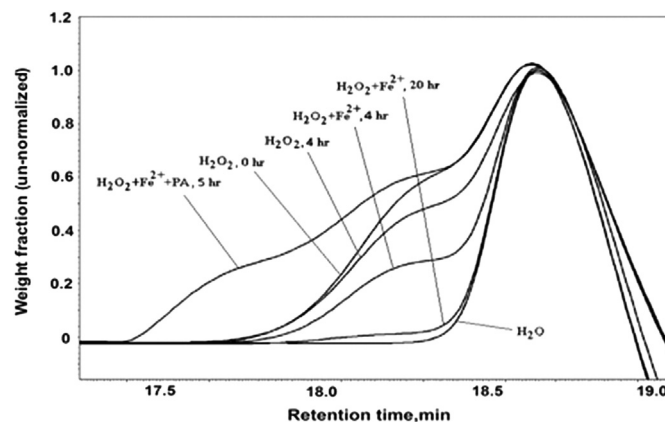


Fig. 1. SEC spectra for hydrogen peroxide decomposition at 68 °C with and without ferrous ions (4 ppm) in the presence and absence of phosphoric acid.

phosphoric acid may have several effects. First of all, the phosphoric acid is a complexing agent for metal ions. At the same time, precipitation of iron phosphates may also occur due to its very low solubility (with a solubility product of 1.3×10^{-22}) resulting in further removal of the ferrous ions and hence inhibiting to the H_2O_2 decomposition. Another effect of phosphoric acid on the peroxide stability is the decreased pH value of the solution. The pH value of pure hydrogen peroxide is 6.2 and slightly lower in diluted solutions. For the stability purpose, commercial hydrogen peroxide solutions are generally adjusted to a pH value below 5, above this value, the decomposition of hydrogen peroxide increases sharply. These effects of phosphoric acid on the inhibited decomposition of hydrogen peroxide were confirmed by the SEC test. As seen from Fig. 1, for the Fenton solution containing phosphoric acid, the peroxide peak at 18.2 min remained almost unchanged even after 5 h.

3.2. Weight losses during the Fenton test

Fig. 2 shows the weight losses of PBI membranes with different molecular weights during the Fenton test. A steady decrease in mass of PBI membrane samples was observed during the test. The weight loss was significantly larger for the membranes with an initial low molecular weight. For PBI membranes with an initial weight of 23,700, for example, the weight loss was about 35 wt% after 100 h of the Fenton test, while the weight loss was only 10–12 wt% for PBI membranes with an initial molecular weight of above 66,000. As a comparison, Nafion 117 membranes had a weight loss of 2.5 wt% after the same period of the test. Lobato et al. observed the same tendency [34].

3.3. Effect of phosphoric acid

The conductivity of PBI membranes is achieved by phosphoric acid doping, which means that in PBI cells phosphoric acid is always present. Most of previous studies on oxidative degradation of PBI membranes under the Fenton test conditions were, however, conducted in the absence of phosphoric acid [27–31] while Chang et al. [32] observed a stabilizing effect of phosphoric acid. Fig. 3A shows the results of Fenton tests in 3 wt% H_2O_2 solution containing 4 ppm ferrous ions at 68 °C. For the Fenton test in the absence of phosphoric acid, one finds that, after 280 h of the test, the PBI membrane lost around 23% of the initial weight. When phosphoric acid was

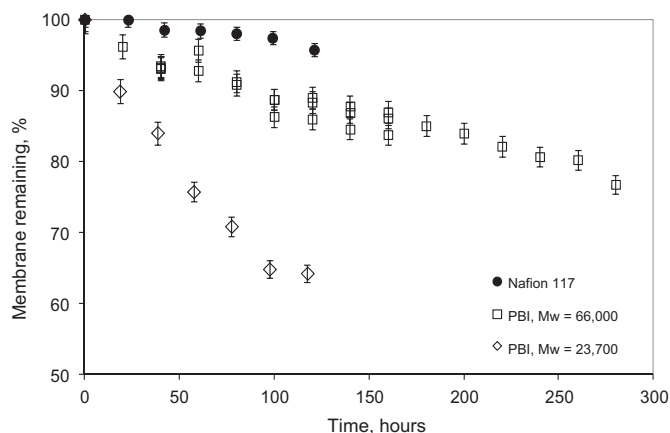


Fig. 2. Weight losses of PBI and Nafion membranes immersed in the Fenton solution consisting of 3 wt% H_2O_2 and 4 ppm Fe^{2+} at 68 °C. The initial molecular weight of PBI membranes was indicated in the figure. The Fenton solution was replaced with a fresh one every 20 h during the Fenton test.

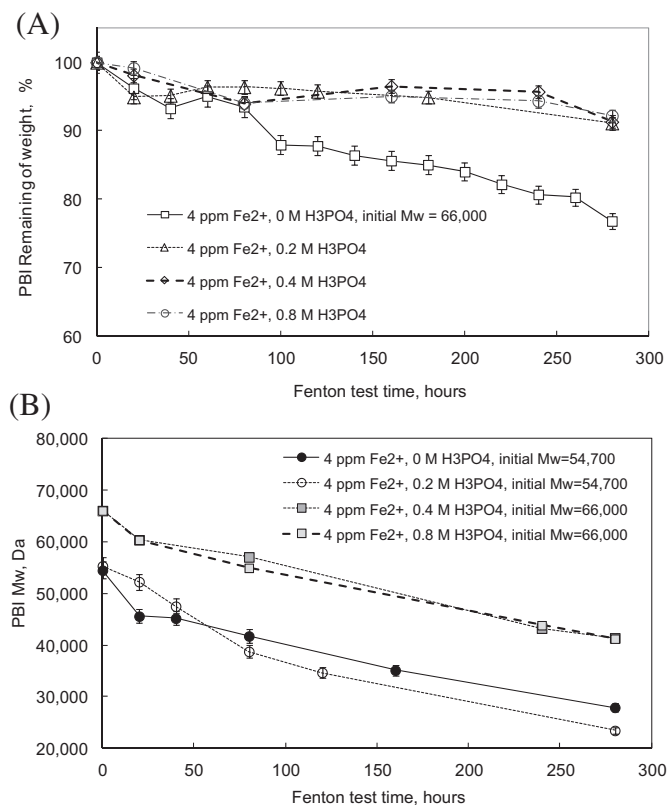


Fig. 3. (A) Weight losses of PBI membranes immersed in the Fenton solution consisting of 3 wt% H_2O_2 and 4 ppm Fe^{2+} at 68 °C in the absence and presence of phosphoric acid. (B) Effects of phosphoric acid on the molecular weight of PBI during the Fenton test. Concentrations of phosphoric acid and ferrous ions in the Fenton solution are indicated in the figure.

added in a concentration of 0.2 M in the Fenton solution, the membrane weight loss was dramatically reduced to about 5 wt%. Further addition of phosphoric acid from 0.2 to 0.8 M H_3PO_4 did not seem to change the membrane degradation. It is also interesting to note from Fig. 3A that, after an initial loss of 5% during the first 20 h, the weight of membranes remained nearly unchanged in the following period from 50 to 280 h.

As discussed above, phosphoric acid inhibits the decomposition of H_2O_2 and therefore the formation of hydroxyl radicals by means of metal ion complexing, phosphate precipitation and decreased pH. At the same time, phosphoric acid present in the Fenton solution is also involved in acid–base interactions with the N–H groups of PBI, as proposed by Chang et al. [32]. The so-called acid doping process has been extensively investigated [35,36], showing that submersion of a PBI membrane in 65–75 wt% H_3PO_4 at room temperature results in an acid uptake of about 5–6 mol H_3PO_4 per molar repeat unit of the polymer. The doped acid leads to a volume swelling of about 100–120% on basis of the dry membrane. In a dilute acid solution e.g. 0.2 M H_3PO_4 , an acid uptake of as high as 0.6 mol H_3PO_4 per molar polymer repeat unit has been reported [36], corresponding to 16 wt % of the acid in the dry polymer. As proposed [27], the polymer degradation under Fenton test conditions started by the attack of hydroxyl radicals at the carbon atom linking the imidazole ring and the benzenoid ring. The acid–base interaction between the phosphoric acid molecules and nitrogen atoms of the imidazole rings, on one hand, might impede the attack of radicals. On the other hand, the resultant membrane swelling would significantly expand the polymer chains and make the radicals more accessible to attack the inner part of polymer membranes.

The SEC analysis was conducted to investigate the molecular weight decrease of the polymer membranes during the Fenton test, as shown in Fig. 3B. A set of data for membranes with an initial M_w of 54,700, as an example, were also listed in Table 1. As seen from the table, a fast decrease in the molecular weight was observed within the first 40 h for the test in the absence of phosphoric acid. Within the following period, a steady decrease in the M_w occurred from ca. 45,000 at 40 h to ca. 28,000 at 280 h. When phosphoric acid was added to the Fenton solution, a slower start of the M_w decrease was observed, followed by a faster and steady decrease in the following period of up to 200 h. It should be remarked that this was achieved at the low phosphoric acid content (0.2 M). As seen from the weight loss data discussed above, the phosphoric acid content may not play a critical role in the molecular weight decrease, however no direct data of higher phosphoric acid contents were available for the M_w 54,700 sample.

A similar trend could be seen for the polymer membranes with an initial M_w of 66,000, as shown in Fig. 3B, where the phosphoric acid contents were 0.4 and 0.8 M, respectively. In this acid range, no noticeable difference could be seen in the measured M_w variations, which most likely were all within the experimental error range.

In addition, in the presence of phosphoric acid, the Fenton tests with and without ferrous ions in the peroxide solution showed little difference in changes of M_w during the test period. As discussed in Fig. 3A, the mass of PBI membranes was steadily decreasing with the time of the Fenton test, while it remained more or less constant in the presence of phosphoric acid. On the other hand, the molecular weight of PBI membranes was found to steadily decrease both in the presence and in the absence of phosphoric acid in the Fenton test solution, as revealed by the SEC shown in Fig. 3B. This may indicate different polymer degradation mechanisms when phosphoric acid was present in the Fenton test solution, as will be discussed in the following section.

3.4. Stability of amino and carboxylic acid groups in the presence of phosphoric acid

Based on the FTIR spectroscopic and other studies, as proposed previously [27], the PBI oxidative degradation under Fenton test conditions was a result of attacks of radicals at the carbon atom linking the imidazole ring and the benzenoid ring, leading to formation of hydroxyl, carbonyl and carboxyl groups and eventually the ring opening. The chain scission generates small molecules and terminal groups that are further oxidized by an endpoint oxidation. In other words, the chain scission would lead to a decrease in the polymer molecular weight and the formation of additional terminal groups, whereas the endpoint oxidation would result in a direct weight loss.

Table 1

Variation of the weight average molecular weight (M_w), number averaged molecular weight (M_n) and the polymer dispersion index (PDI) of PBI membranes during the Fenton test without and with the presence of phosphoric acid (in concentration of 0.2 M).

| | Fenton test duration | | | | | |
|---|----------------------|--------|--------|--------|--------|--------|
| | 0 h | 40 h | 80 h | 120 h | 160 h | 280 h |
| 3 wt% H ₂ O ₂ + 4 ppm Fe ²⁺ | | | | | | |
| M_w | 54,700 | 45,600 | 41,700 | — | 35,100 | 27,900 |
| M_n | 28,700 | 21,900 | 21,100 | — | 18,900 | 15,700 |
| PDI | 1.9 | 2.08 | 1.97 | — | 1.85 | 1.78 |
| 3 wt% H ₂ O ₂ + 4 ppm Fe ²⁺ + 0.2 M H ₃ PO ₄ | | | | | | |
| M_w | 55,300 | 47,500 | 38,700 | 34,700 | — | 23,200 |
| M_n | 29,100 | 23,900 | 20,600 | 18,900 | — | 13,500 |
| PDI | 1.9 | 1.99 | 1.89 | 1.83 | — | 1.71 |

From a synthetic point of view, the two major terminal groups of PBI macromolecular chains are the amino N–H and carboxylic acid groups (–COOH). The relative stability of the two groups was investigated by the Fenton test of the two monomers for PBI synthesis, 3,3'-4,4'-tetraaminobiphenyl (TAB) bearing basic amino groups and isophthalic acid (IPA) bearing carboxylic acid groups. Fig. 4 shows the FTIR spectra of the two monomers before and after the Fenton test. For IPA, the characteristic absorption bands at 1700 and 1280 cm^{−1} were attributed to the stretching vibration of the C=O bond and C–O bending vibration, respectively. A band at 1340 cm^{−1} in the spectra was related to the aromatic ring vibration of IPA. For TAB, the band at around 3300 cm^{−1} was attributable to the stretching vibration of N–H in the benzimidazole ring. Furthermore, the bands at 1570 and 1630 cm^{−1} were assigned to the stretching vibration of aromatic rings. After the Fenton oxidation of IPA, there was only a slight increase of the band at 1700 cm^{−1} and a slight decrease of the band at 1280 cm^{−1}, showing little structural change of the remaining monomer during the Fenton test. For TAB, however, the characteristic bands disappeared or significantly decreased after the Fenton test.

As mentioned above, the hydrogen peroxide solution is chemically acidic and any acid–base interaction with the peroxide would stabilize the amino groups during the Fenton test. As previously suggested [27], this acid–base interaction might be the major difference between the oxidative degradation of PBI under the Fenton radical attack and the thermal oxidation by atmospheric dioxygen. And this interaction is of more significance when phosphoric acid is present. In other words, the strong acid–base interaction between the phosphoric acid molecules and amino terminal groups might impede the attack of hydroxyl radicals during the polymer membrane degradation test, as seen from the decreased weight loss and molecular weight reduction during the Fenton test in Fig. 3.

3.5. Fuel cell durability test in the presence of ferrous ions

As rationalized above, PBI membranes are used as fuel cell electrolytes in the acid doped form. The acid doping levels are typically in a range of 5–6 mol H₃PO₄ per repeat unit of the polymer, which is a result of a compromise between proton conductivity, mechanical strength and gas permeability. By means of high molecular weight polymer, covalent/ionic cross-linking [31,37] or inorganic–organic composite [38] membranes, higher acid doping levels can be achieved with sufficient mechanical strength, improved dimensional stability or reduced membrane swelling. Typically an acid doping level of as high as 9–11 mol H₃PO₄ was used for the cross-linked [31] as well as composite [38]

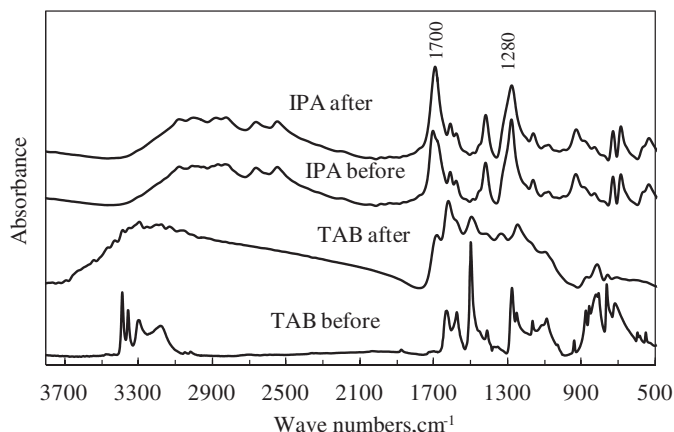


Fig. 4. FTIR spectra of TAB and IPA before and after 20 h of the Fenton test.

membranes. Using an alternative method for direct casting PBI membranes from a polymer solution in polyphosphoric acid (PPA), the so called sol–gel process, PBI membranes may have acid doping levels of as high as 20–40 mol H_3PO_4 per polymer repeat unit [39–43]. Under these circumstances the effect of phosphoric acid, which is far beyond the concentration range of the present study, on the polymer membrane degradation can be of more importance.

With PBI membranes doped to an acid level of 11 mol H_3PO_4 , two MEAs were fabricated from electrodes without and with impregnation of ferrous ions. Durability tests were conducted at a constant current density of 300 mA/cm^2 at 160°C under operation with dry hydrogen and air. As shown in Fig. 5, the MEA with PBI reference membranes showed a slight yet steady increase in the cell voltage during the first 500 h. For the present study, the gas diffusion electrodes were fabricated by spraying a catalyst ink containing catalyst, PBI but not phosphoric acid. The phosphoric acid that was needed for doping the PBI binder in the catalyst layer was from the acid doped membranes. In this case, the MEA performance during a constant current density operation typically showed a slow activation process at the start. The overall cell voltage performance in the test period of 1554 h exhibited no noticeable degradation.

At the start (0 h) and end (at 1554 h) of this test period, I – V polarization curves were recorded. The measured cell voltage in the region of current density, where no significant contribution of the mass transportation was present, can be expressed as:

$$E = E_{i=0} - iR - b \log i \quad (8)$$

Here $E_{i=0}$ is the open-circuit voltage (OCV), iR is the ohmic loss primarily due to the membrane resistance, and the logarithmic term is the voltage loss due to kinetic polarization of electrodes. A regression analysis based on the above expression divided the I – V curves into the two specific terms of iR -free polarization and ohmic loss, as shown in Fig. 6. As seen from the figure, even though the overall polarization curves showed little changes for PBI reference MEAs during the test period of 1554 h, a slight improvement of the kinetic polarization and an increase in the ohmic voltage loss were observed. The specific ohmic resistivity of the cell was found to increase from $0.28 \text{ } \Omega \text{ cm}^2$. By assuming that the ohmic loss is due to the membrane resistance, these values correspond to a membrane proton conductivity of 0.047 and 0.041 S cm^{-1} , respectively, using the thickness of the acid doped membrane of 130 microns. The values are slightly lower than the reported membrane conductivity, most likely due to other ohmic contributions from catalyst layer, gas diffusion layer, current collectors and

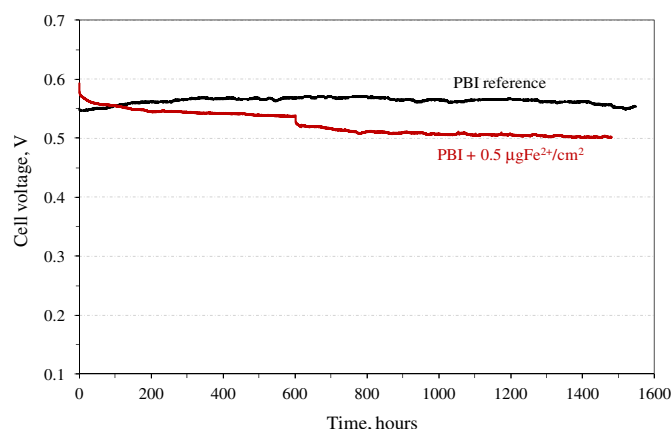


Fig. 5. Cell durability in term of cell voltage at 300 mA cm^{-2} at 160°C with phosphoric acid doped PBI membranes in the absence and presence of ferrous ions.

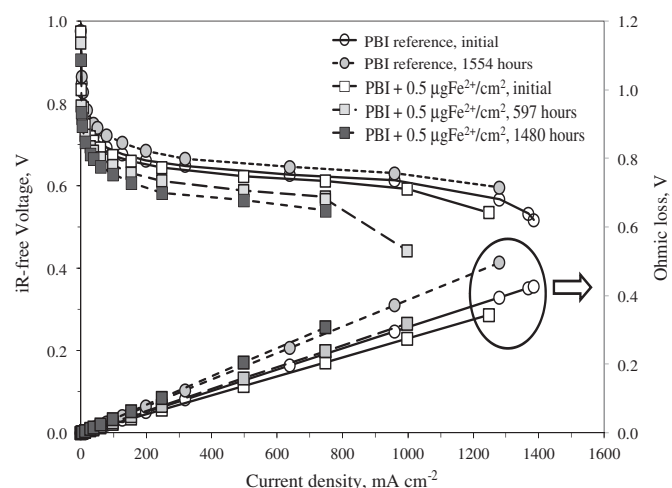


Fig. 6. IR-free polarization and ohmic voltage losses of the durability test cells. Both membranes were prepared from polymers with molecular weights of about 50,000 and doped to an acid level of about 11 mol H_3PO_4 per repeat unit of the polymer. The Pt loading of each electrode was 0.58 mg cm^{-2} . The ferrous ions were impregnated into the catalyst layer of electrodes at a content of $0.5 \text{ } \mu\text{g Fe}^{2+} \text{ cm}^{-2}$. Both cells were operated with unhumidified H_2 and air.

connections in fuel cells. This is not surprising for the MEAs of the present study because the doping acid in the membrane would slowly transfer into the catalyst layer during the test, which, in turn, improved the electrode kinetics at expense of decreased conductivity of the membrane.

For the MEA containing $0.5 \text{ } \mu\text{g Fe}^{2+} \text{ cm}^{-2}$ on the electrode surface, instead of the initial slow improvement of the cell performance for the PBI reference MEAs, a performance degradation was observed during the first 100 h of the durability test, followed by a steady decrease in the subsequent period. An interruption of the durability curve occurred at 597 h when an I – V polarization curve was recorded. This was unusual in the durability tests where 24 parallel fuel cells with varied types of membranes and electrodes are continuously operating in the laboratory. Anyhow, the slow yet steady performance degradation was continued in the following period of up to 1480 h when the third I – V polarization curve was recorded. The three polarization curves were presented in form of iR -free cell voltage and ohmic loss in Fig. 6. The calculated specific ohmic resistivity from the polarization curves was $0.31 \text{ } \Omega \text{ cm}^2$ at the start, $0.39 \text{ } \Omega \text{ cm}^2$ at 597 h, and finally $0.41 \text{ } \Omega \text{ cm}^2$ at the end (1480 h) of the durability test. This is in good agreement with the trend of the PBI reference membranes, though with a higher increasing rate than that for the PBI reference, showing no significant membrane degradation. On the other hand, a significant increase in the iR -free cell voltage, i.e. the kinetic polarization, was observed during the durability test. Moreover additional, deterioration of the I – V curves was observed in the current density range higher than 700 mA cm^{-2} , indicating the increased mass transfer resistance most likely from the catalyst layers of electrodes.

Recently Li et al. [44] reported a study on the effect of Fe^{3+} and Al^{3+} contamination, as injected in the air stream, on the cathode performance of a Nafion based PEMFC. They showed both increases in the kinetic and mass transfer resistances, which were greater contributors to the cell performance than the increase in the membrane resistance, though the formation of membrane pinholes eventually caused a sudden death of the cell. In the present study, the impregnated ferrous ions would be oxidized to Fe^{3+} immediately at the cathode side. It seems that the catalyst deterioration was the major effect of the ferrous ion contamination whereas no noticeable effect on the membrane degradation was observed in the

present study. This seems supporting the result of the membrane Fenton tests in the presence of phosphoric acid, which was found to stabilize the polymer membranes under the oxidative attack of radicals. Caution should be taken, of course, in translating the Fenton test results into the fuel cell durability, particularly with respect to effects of ferrous ions and phosphoric acid. In fuel cells peroxide radicals are generated at the catalytic sites of the electrode–membrane interface and therefore might behave very differently as compared to solutions. This is however a general issue in developing protocols for membrane evaluation of both low temperature and high temperature PEMFCs.

4. Conclusions

Oxidative degradation of PBI membranes under Fenton test conditions were investigated by measurements of the weight loss, intrinsic viscosity and SEC with emphasis placed on effects of phosphoric acid and ferrous ions. Introduction of ferrous ions into the Fenton reagent accelerated the formation of peroxide radicals and hence the polymer degradation in terms of weight loss and molecular weight decrease. The presence of phosphoric acid as the dopant of membranes, on the other hand, was found to significantly inhibit the polymer degradation by suppressing the radical attack possibly via metallic ion complexing and decreased pH as well as acid–base interaction with the amino groups of the polymer. Fuel cell durability tests with contamination of ferrous ions at the interface between the membrane and electrodes showed significant performance degradation primarily due to the catalytic deterioration rather than the membrane degradation, further verifying the positive effect of phosphoric acid on the polymer stability in fuel cells.

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